Pretreatment of Bauxite With Hydrogen

By D. J. MacDonald, K. R. Sandgren, M. J. Zamzow,
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	$lb/(h \cdot ft^2)$	pound per hour per square foot
cm^2	square centimeter	mg/L	milligram per liter
cm/h	centimeter per hour	min	minute
°C	degree Celsius	mL	milliliter
°F	degree Fahrenheit	mL/cm^2	milliliter per square centimeter
ft	foot	mL/min	milliliter per minute
g	gram	mm	millimeter
g/L	gram per liter	mt	metric ton
G	gauss	pct	percent
h	hour	psig	pound per square inch, gauge
in	inch	rpm	revolution per minute
in Hg	inch of mercury	s	second
kW·h	kilowatt hour	Torr	torr
L	liter	wt pct	weight percent

PRETREATMENT OF BAUXITE WITH HYDROGEN

By D. J. MacDonald,[1] K. R. Sandgren,[2] M. J. Zamzow,[2]
R. P. Bush,[3] and D. E. Shanks[4]

ABSTRACT

As part of a U.S. Bureau of Mines program seeking improvements to the Bayer process, a typical Jamaican bauxite was heated at temperatures up to 500° C in hydrogen, and its leachability under Bayer process conditions was measured and properties of its leached residue were observed. The objectives were to find ways to decrease the amount of organic carbon in bauxite or in leach liquor derived from it without impairing its leachability, and to improve the leached residue's filterability. Techniques employed included heating bauxite under pressure in an autoclave with hydrogen, and in flowing hydrogen at ambient pressure in a tube furnace. Leaching tests were done with a 600-mL stirred reactor. In some of the leaching tests, ferrous sulfate ($FeSO_4$) was introduced before leaching to produce a partially magnetic product. Results showed that exposure to hydrogen at temperatures from 160° to 360° C progressively diminished the bauxite's content of organic carbon and decreased the ratio of organic carbon to aluminum in leach liquor, an improvement that would allow a process using hydrogen-treated bauxite to be operated at a smaller recycle ratio, thereby consuming less energy and allowing greater throughput for a plant of given capacity. The bauxite's leachability was not impaired by high-temperature pretreatments, except at temperatures higher than 280° C. Pretreatments in hydrogen produced black, partially reduced bauxite which upon leaching gave a residue that was attracted to a magnetic field and was amenable to separation from green liquor by a magnetic filtration method.

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INTRODUCTION

Aluminum is now the predominant nonferrous metal, outranking copper in annual tonnage of production in the United States and worldwide. Only iron and steel are produced in greater quantity than aluminum. In 1988, domestic refineries produced 3.94 million mt of aluminum (1).[5] Production of alumina (Al_2O_3) in the United States in 1988 amounted to 5.1 million mt, or 2.7 million mt expressed as aluminum equivalent. This compares with worldwide production of alumina in 1988 of 37.4 million mt (2). In addition to their economic importance, aluminum and its precursor alumina have considerable strategic importance. Aluminum alloys are extensively used in construction of military aircraft, naval vessels, guided and ballistic missiles, and other weapons and vehicles.

Bauxite is the main source of alumina, through the process first developed by the Austrian scientist Karl Bayer more than 100 years ago. Through the years, many technological improvements have been made in the Bayer process, but the basic procedure has remained unchanged. It involves a caustic leach of bauxite at elevated temperature and pressure, followed by separation of the resulting sodium aluminate solution (green liquor) from the leached residue (red mud or brown mud), and precipitation of the aluminum as hydrated aluminum oxide ($Al_2O_3 \cdot 3H_2O$), also called alumina trihydrate, which is calcined to alumina. The caustic leach, or digestion, requires up to 5 h at 220° to 550° F (104° to 288° C) and caustic concentrations from 200 to 300 g Na_2CO_3 (sodium carbonate) equivalent per liter. Exact conditions depend on the nature of the bauxite being processed, and conditions used in a given Bayer process plant are usually tailored to a particular type of bauxite. Research reported here was based on a bauxite of Jamaican origin, typical of the bauxite commonly processed in a major U.S. plant.

The Bayer process is energy intensive, largely because solutions being recycled within the process must be reheated at each pass and the recycle ratio is large. The energy required to produce alumina has been reported (3) to be 5,600 kW·h equivalent per short ton. Heat energy required to reheat the spent liquor per unit of alumina production is proportional to the recycle ratio, which is typically two or more. The large recycle ratio is dictated by the incompleteness of precipitation of alumina trihydrate when green liquor is cooled and seeded. Any circumstance that interferes with alumina trihydrate precipitation leads to larger recycle ratios and greater energy consumption. Jamaican bauxite typically contains 0.2 pct organic carbon, principally as humates and fulvic acid salts, etc., which presumably originated from decay of plants growing in soils above the water-permeable bauxitic soil horizon. During Bayer leaching, this organic matter undergoes degradation to oxalate, which is resistant to further degradation. The oxalate therefore accumulates in the circulating Bayer liquor, reaching an organic carbon concentration of 9 g/L or more. Its presence slows the precipitation of alumina trihydrate and tends to produce alumina that is off specification with regard to its particle size and bulk density. It can also precipitate as sodium oxalate, which interferes with filtration.

Another major problem is the separation and disposal of leached solids, known as red mud. For each short ton of alumina produced, a short ton or more of red mud solids, predominantly goethite, is discharged as settler underflow (a slurry) at a solids content of 20 to 30 pct. It is caustic, slimy, thixotropic, excruciatingly slow to settle, virtually impossible to filter, and has a repulsive odor. At a solids content up to about 30 pct it can be pumped, and at a solids content above about 60 pct it can be handled as a self-supporting solid. At intermediate levels of solids content, it can be neither pumped nor shovelled, nor will it support a load. After impoundment for several years under a humid Gulf-coast climate, it settles to about 50 pct solids, but will not sustain the load of buildings or motor vehicles.

This U.S. Bureau of Mines investigation had three objectives: to improve the process' energy efficiency by removing or altering the organic matter in bauxite or Bayer leach liquor, to improve the settling or dewatering of leached residue, and to improve the clarification of green liquor. The general approach was to treat bauxite with hydrogen before leaching in the hope of altering or eliminating its organic matter, or changing its physical characteristics so that the leached residue could be more readily separated from the leach liquor, and to make the leached residue amenable to magnetic separation.

In this report, the term *pretreatment* refers to processing that was followed by Bayer leaching to produce a slurry or a residue, and the term *treatment* refers to processing not related to Bayer leaching.

Treatment of bauxite and/or leached bauxite slurries by oxidation has been described (4-6), but treatment of bauxite in hydrogen has not been described elsewhere.

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[5]Italic numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENTAL WORK

MATERIALS

Bauxite used in this investigation was a typical Jamaican bauxite, high in goethite, and was obtained from Kaiser Aluminum and Chemical Corp., Baton Rouge, LA.[6] The bauxite was crushed and screened to minus 10 mesh, and was blended for uniformity. Its composition is given in table 1, wherein each element except carbon is reported as the oxide. Its mineralogical composition was not determined. Calcium in this bauxite occurs primarily as calcium carbonate.

Gases used were hydrogen, ultra high purity, 99.999 pct, and helium, Bureau's high purity helium, 99.997 pct.

Starch used as a flocculant was ordinary kitchen-type cornstarch. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) reagent grade, was used as a reducing additive. Sodium hydroxide used in leaching tests was reagent grade.

Table 1.—Composition of bauxite used in this work

Component:	Wt pct
Al_2O_3	44.2
Fe_2O_3	16.4
TiO_2	2.3
CaO	1.1
SiO_2	.57
MnO	.46
P_2O_5	.42
MgO	.06
Organic carbon[1] ..	.22
Loss on ignition (H_2O + CO_2) ...	33.6

[1]Average organic carbon content was 0.224±0.014 pct.

EQUIPMENT AND PROCEDURE

Pressure Treatment

Treatments of bauxite under pressure without added liquids were carried out with a Parr Model 4022 rocking pressure reactor electrically heated and having an internal volume of 1 L. Bauxite was treated in 250-g batches, under hydrogen or helium gas introduced under pressure before heating began. Except as stated otherwise, the loaded reactor was brought to the desired temperature, held at that temperature for a predetermined period (usually 6 h), and allowed to cool to room temperature

overnight before gas pressure was released and the reactor's solid contents removed. For analysis of its organic carbon content, a representative portion of the treated bauxite batch was ground to minus 60 mesh and thoroughly mixed before analysis. Ratios of ferrous to ferric iron were determined by a wet chemical method.

Ambient Treatment

A 1-in (nominal) by 12-in Lindberg tube furnace placed vertically was used for treatment of bauxite in flowing hydrogen at ambient pressure. The vertical position was used to avoid shifting of the bauxite bed that would allow flowing gas to bypass the sample. A supported 28-mm OD Pyrex glass tube was used to hold 50-g samples of minus-10 plus-40 mesh bauxite. Fines smaller than 40 mesh were excluded to avoid impeding the flow of gas through the bed of bauxite. The bauxite was supported in the tube by a 7-in bed of sand, which also served to preheat the gas. A sheathed type K thermocouple was centered in the sample. The gas flow rate was about 50 mL/min.

In addition, some hydrogen treatments of bauxite at atmospheric pressure were done with the bauxite held in alumina boats in a three-zone Lindberg tube furnace with the boats placed inside an alumina tube. Temperature was monitored with a thermocouple placed inside the tube over the middle portion of the heating zone.

Leaching Tests

Leaching tests were done in a Parr 600-mL stirred autoclave in which 60 g of sample was reacted with 390 mL of 2.71N NaOH. The tests were run at 250° C for 2 h with a 45-min warmup time. The stirring speed was 550 rpm. After leaching was complete, the reactor and its contents were either allowed to cool to 90° C or were quenched under cold water to 25° C before the leached slurry was removed from the reactor.

Leached residues were also produced in a partially reduced condition by addition of $FeSO_4$ to untreated bauxite in a leaching procedure which was otherwise the same as that described previously.

Magnetic Separation

Magnetic susceptibilities of hydrogen-treated samples were measured using a Johnson-Matthey magnetic susceptibility balance after being ground to minus 60 mesh. Some of the samples had magnetic susceptibilities beyond the range of the instrument. Those samples were diluted

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[6]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

by grinding with raw bauxite in a ratio of 1 part sample to 5 or 10 parts untreated bauxite before magnetic susceptibility measurement.

Magnetic separation methods were examined in an attempt to exploit the increased magnetic susceptibility imparted by hydrogen treatment of bauxite at elevated temperatures. Samples of bauxite were given hydrogen pretreatment at a series of elevated temperatures, then leached to produce a series of leached residues. The leached residues, representing a wide range of magnetic susceptibilities, were used in magnetic separation tests.

The magnetic separation apparatus (fig. 1) consisted of a Carpco electromagnet (which develops 2,500+ G), and a glass tube 150 mm long by 22 mm ID inserted between the magnet's pole pieces and filled with approximately 10 g of coarse (No. 3) steel wool. The glass tube was placed in the magnetic field at an angle of approximately 45° from the vertical to allow gravity-assisted drainage. A glass funnel and Tygon tubing with a screw clamp to regulate the flow was attached to the glass tube and elevated above the tube.

A 250-mL portion of a slurry of leached bauxite residue and leach liquor was passed through the bed of steel wool at a controlled flow rate of 20 mL/min with the electromagnet at maximum amperage. The clarified liquor was collected in a 500-mL Erlenmeyer flask, and solids were retained on the steel wool. A slight vacuum (approximately 150 Torr) was applied until no further liquid drained from the steel wool. The loaded steel wool was weighed, dried in an oven at 50° C, and weighed again to determine the collected solids' moisture content.

The amount of suspended solids remaining in the liquor after magnetic separation was also determined. This was done by passing a portion of the clarified liquor from a magnetic separation test performed on leached bauxite pretreated with hydrogen at 360° C for 6 h, through a piece of Zitex fluorocarbon polymer filter paper. Solids captured on the filter paper were dried and weighed.

Organic Carbon Determination

Carbon in the form of organic compounds contained within the bauxite, as distinct from carbon present as calcium carbonate ($CaCO_3$), was determined by a LECO Model CS-125 carbon-sulfur determinator, which was calibrated against a LECO standard for carbon in soil, part No. 502-602, lot No. 586. Carbonate carbon was removed from bauxite samples for carbon analysis by a pretreatment with dilute H_2SO_4 and drying before carbon analysis.

Leached bauxites

KEY

A Glass funnel
B Tubing
C Pinchcock
D Electromagnet
E Glass tube connector
F Glass tube filled with steel wool
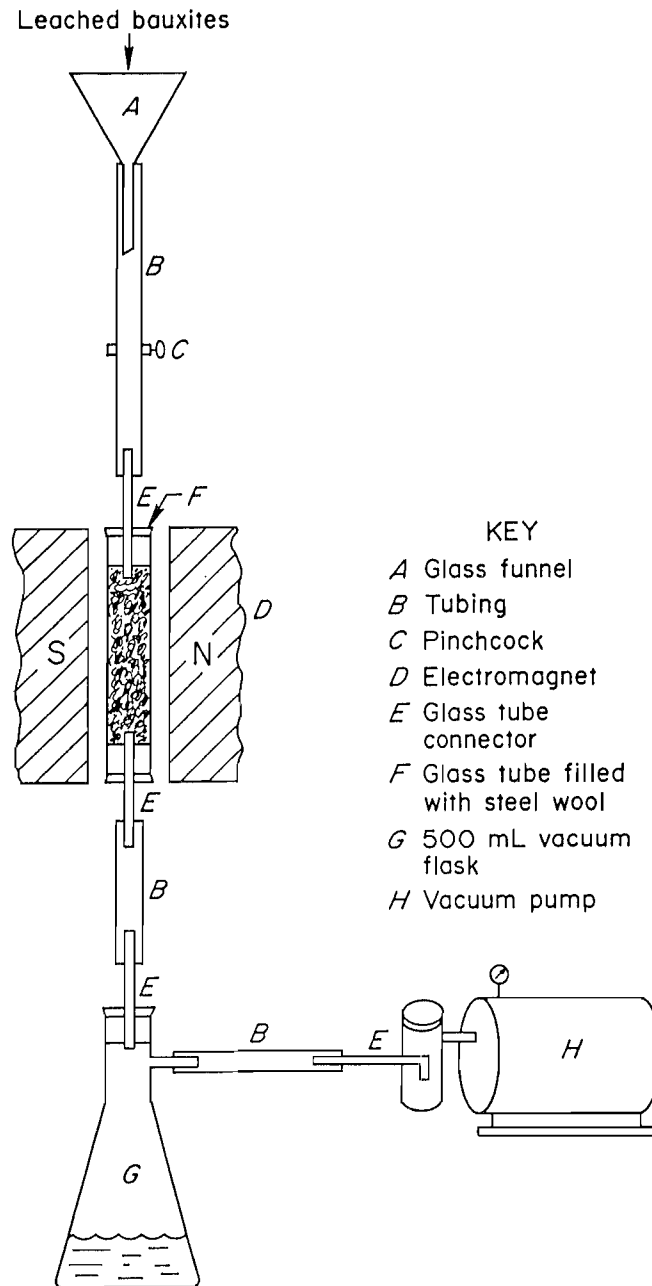G 500 mL vacuum flask
H Vacuum pump

Figure 1.—Magnetic separation apparatus.

Gas Chromatography

Analysis of gaseous products produced from treatments of bauxite at elevated temperature and pressure was done with a Hewlett-Packard Model 5710A gas chromatograph using a thermal conductivity detector, a 7-ft by 1/8-in 13X

Mole Sieve column, and helium carrier gas. One such treatment and subsequent gas chromatographic analysis was performed on acid-treated bauxite. The bauxite was soaked in dilute acid and gently dried, thereby eliminating carbonate from the bauxite, before its elevated temperature treatment in hydrogen.

Settling and Filtration Rates

To flocculate selected samples of leached slurry in connection with settling rate tests, 11 mL of starch solution was added to 400 mL of unwashed slurry. The starch solution was prepared by adding 2 g starch to 20 mL of wash water from a previous leaching test, boiling the mixture for 10 min, and diluting with water by a factor of 10. The starch solution was added slowly while gently stirring the slurry for 10 s.

Tests were done to determine the effect of pretreatment and digestion conditions on the filterability of Bayer muds. A top feed test was used in which slurry of known volume and weight was mixed in an Erlenmeyer flask to ensure a homogeneous mixture and quickly poured into a Buchner funnel fitted with glass fiber filter paper. A 10-in Hg vacuum was then applied, and the filtration time and the thickness of the filter cake were recorded. The cake was washed with water and dried in an oven at 100° C and weighed to determine the initial slurry concentration. From these data, the form filtration rate was computed. Organic carbon was determined on the dried residue in some cases.

Several unwashed slurries from leaching of hydrogen-pretreated bauxite were magnetically flocculated before settling. The flocculation was done by pouring 400 mL of slurry through a tube that had been placed at the center of a doughnut-shaped permanent magnet.

Magnetic Separation Tests (Eriez)

Magnetic separation of leached residues derived from hydrogen-treated bauxite was investigated with an Eriez Model L-4 wet high intensity magnetic separator (WHIMS). This was done by personnel of Eriez Magnetics in their applications laboratory at Erie, PA.

The Eriez Model L-4 WHIMS consisted of two electromagnet coils operating at 26.3 A on two flux-converging elements acting on a pole box 8-in high by 2-in deep by 1-in wide.

Trial and error testing on a bench-scale WHIMS at the Eriez laboratory showed that a stainless steel wool matrix was the most effective separation medium. Further testing using a single WHIMS matrix cell 8-in high by 1-in wide by 2-in deep packed with "standard" grade stainless wool (Eriez' terminology) to a density of 5 pct demonstrated that 100 mL/min was the maximum flow rate of bauxite slurry from bauxite pretreated in hydrogen under pressure at 380° C that could be completely separated at a field strength of 2,500 G. This flow rate (100 mL/min) was then adopted as standard for all other WHIMS tests. The "standard" grade stainless steel wool is a mixture of grades with an average coarseness similar to coarse No. 3 commercial grade steel wool of ordinary mild steel.

Residue selected for use in magnetic separation tests was derived from bauxite which had been treated in hydrogen at 380° C because that was the temperature at or near optimum for producing magnetic susceptibility in the bauxite. This is not to imply that 380° C would be optimum from the standpoint of the overall alumina production process.

Breakthrough tests were performed to find the loading capacity of the steel wool at magnetic field strengths of 2,500, 5,000, and 7,500 G. WHIMS rarely employs fields larger than 8,000 G. These tests were performed by passing through the WHIMS cell an increasingly large portion of leached slurry until the clarified liquor emerging from the cell changed from clear to slightly colored. The slightly colored liquor contained approximately 10 to 15 mg/L of suspended solids.

RESULTS

TREATMENT IN HYDROGEN UNDER PRESSURE

Treatment of bauxite at elevated temperature with an ample quantity of hydrogen gas in a closed autoclave decreased the bauxite's organic carbon content. Figure 2 shows results as a function of treatment temperature. Temperature lower than 160° C produced negligible loss of organic carbon. The highest temperature used, 460° C, yielded the lowest organic carbon, 0.036 pct.

GASEOUS REACTION PRODUCTS

The observation that bauxite lost organic carbon when heated in hydrogen raised the question of whether the effect was caused by chemical reaction or merely thermal decomposition. To answer this question, experiments were performed in which bauxite was heated in helium under pressure. Since helium is not chemically reactive, any carbon-bearing gaseous products could only be the result of thermal decomposition, uncomplicated by the reactions
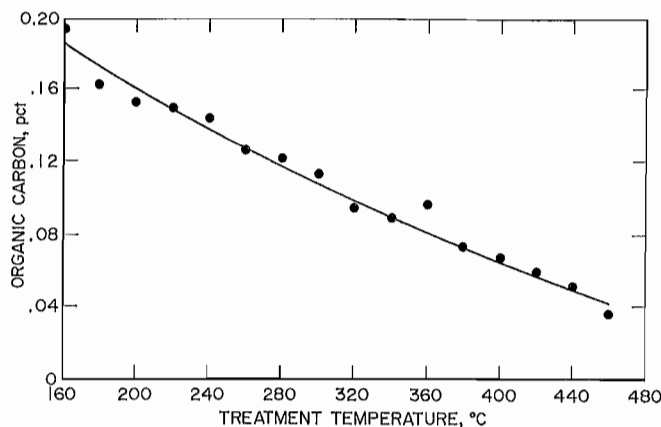
Figure 2.—Organic carbon in bauxite after 6-h treatment in hydrogen under pressure, as function of temperature.

that hydrogen can enter into. Organic carbon levels produced by treatment in helium are shown in table 2, and are similar to organic carbon levels produced by treatment in hydrogen. Water vapor evolved from bauxite upon heating added substantially to the total pressure. Gaseous products (other than water) from treatment of bauxite in helium or hydrogen were collected in gas sampling bottles and analyzed by gas chromatography to detect differences in the nature of reaction products.

Table 2.—Total pressure and organic carbon as functions of temperature for 6-h treatment of bauxite in helium under pressure[1]

Temperature, °C	Pressure, psig	Organic carbon, pct
300	1,320	0.112
350	1,700	.093
400	2,360	.080
450	3,000	.044

[1]Initial helium pressure at 25° C was 200 psig.

Results from gas chromatographic analysis (table 3) indicate the occurrence of decarboxylation of organic acid, in which -COOH groups naturally present in the organic matter of bauxite decompose to yield carbon dioxide and hydrogen. Even the sample from which carbonate had been removed by soaking in acid yielded carbon dioxide upon treatment in hydrogen. That experiment showed that the observed carbon dioxide came from some source other than the thermal decomposition of carbonate. Results also suggest that methane was primarily formed from reaction of hydrogen with carbonate. The presence of hydrogen in the gas produced by heating bauxite in helium agrees with proposed decomposition of -COOH groups to form carbon dioxide and hydrogen. The absence of ethane (C_2H_6) and higher hydrocarbons suggests that hydrogenation of the organic matter adsorbed on bauxite did not occur.

CONVERSION TO MAGNETITE

Hydrogen treatment also converted part of the bauxite's Fe^{3+} to Fe^{2+}, and made the bauxite black and ferrimagnetic, owing to development of magnetite, Fe_3O_4. Table 4 shows numerical data on organic carbon, total pressure developed at the elevated temperature, concentrations of Fe^{2+} and Fe^{3+}, $Fe^{2+}:Fe^{3+}$ ratio, and magnetic susceptibility. A $Fe^{2+}:Fe^{3+}$ ratio equal to 0.5 corresponds to the magnetite composition.

Treatment of bauxite in hydrogen under pressure for a duration shorter than the usual 6-h treatment also caused a decrease of organic carbon content and an increase of $Fe^{2+}:Fe^{3+}$ ratio (table 4).

Settling rates of leached residues from bauxite pretreated in hydrogen under pressure are graphed in figure 3. Six-hour pretreatment resulted in somewhat increased settling rates relative to the 10.9-cm/h settling rate of residue from untreated bauxite, at least for pretreatment temperatures in the range of 200° to 280° C. Pretreatment of shorter duration produced improvements in settling rate, at least in the pretreatment temperature range of 260° to 350° C. Best settling rate was obtained by brief pretreatment (brief means a duration of 1 h or less, in contrast to the usual 6-h duration) about 300° C. Best settling rate for residues from bauxite given 6-h pretreatment in hydrogen correlated with pretreatment temperature of 220° to 240° C. Higher ratios of Fe^{2+} to Fe^{3+} did not necessarily correlate with increased magnetic susceptibility, probably because part of the Fe^{2+}, especially at higher treatment temperatures, was in the form of nonmagnetic iron(II) aluminate ($FeAl_2O_4$). Formation of $FeAl_2O_4$ might also account for part of the decline of aluminum leachability. Greatest magnetic susceptibility obtained in 6-h hydrogen treatments under pressure was produced with a temperature of 400° C and coincided with a $Fe^{2+}:Fe^{3+}$ ratio of 1.68. Treatment for a shorter duration produced a smaller extent of reduction at a given temperature.

LEACHABILITY OF ALUMINUM VALUES

Leaching tests on samples of bauxite subjected to a variety of pretreatments gave results shown in figure 4 and table 5.

Pretreatment in hydrogen under pressure for 6 h caused no loss of aluminum leachability for treatment temperatures up to 280° C. Pretreatment in hydrogen under pressure for durations up to 90 min caused no loss of leachability for pretreatment temperatures up to 340° C.

Table 3.—Composition of gaseous products evolved from bauxite by treatment with hydrogen or helium under pressure,[1] percent

Gas	Treatment conditions Temp, °C	Duration, h	O_2	N_2	CO	CH_4	CO_2	C_2+	H_2	He
Hydrogen	350	6	0.38	1.1	tr	0.22	8.8	0.0	bal	0.0
Helium	300	4	.025	.09	tr	.056	5.3	.0	0.63	bal
Hydrogen[2]	300	4	tr	.09	0.38	.02	6.3	.0	bal	.0

bal Balance. tr Trace.

[1]Initial pressure was 100 psig.

[2]To remove carbonate, bauxite was washed overnight with dilute acid, rinsed with H_2O, and dried at 90° C before treatment with H_2 under pressure.

Table 4.—Organic carbon, total pressure, reduced iron, and magnetic susceptibility in treatment of bauxite with hydrogen under pressure[1]

Treatment duration and temp, °C	Organic carbon, pct	Total pressure, psig	Fe^{2+}, pct	Fe^{3+}, pct	Ratio[2]	Magnetic susceptibility, 10^6 cgs units
6 h:						
160	0.194	600	0.06	13.5	0.004	ND
180	.163	860	.03	13.9	.002	ND
200	.153	930	.07	12.7	.006	ND
220	.149	1,020	.03	13.1	.002	ND
240	.144	1,210	.16	13.4	.012	ND
260	.126	1,290	.43	13.7	.013	57
280	.121	1,370	1.0	13.2	.076	230
300	.113	1,660	2.3	10.8	.21	550
320	.095	1,940	5.1	8.6	.59	1,120
340	.090	2,630	6.2	6.8	.91	1,330
360	.097	2,800	7.1	6.6	1.08	1,470
380	.074	3,150	7.8	5.4	1.44	1,560
400	.068	3,060	8.2	4.9	1.67	1,770
420	.060	3,530	8.5	4.6	1.85	1,500
440	.052	3,730	8.8	4.0	2.2	1,360
460	.036	4,000	9.6	3.2	3.0	1,110
0.9 h:						
258	.143	ND	.05	9.8	.005	22
351	.080	ND	4.0	12.3	.33	555
0.8 h: 385	.063	ND	5.8	7.6	.76	1,430
0.7 h: 339	.095	ND	.65	12.1	.054	86
0.6 h: 296	.138	ND	.05	8.3	.006	35
0.5 h: 436	.051	ND	7.5	5.8	1.29	1,565

ND Not determined. [1]Initial hydrogen pressure at 25° C was 500 psig. [2]Fe^{2+}/Fe^{3+}

In contrast, treatment in hydrogen under pressure for 6-h duration caused significant loss as low as 300° C, and leachability declined to 80 pct at a pretreatment temperature of 360° C and fell to 70 pct at a pretreatment temperature of 380° C. Pretreatment in helium under pressure caused no loss of leachability at temperatures up to 340° C. In contrast, under helium pretreatment, leachability declined to about 86 pct for a pretreatment temperature of 440° C. Pretreatment in hydrogen limited to ambient pressure resulted in no significant loss of leachability even with pretreatment temperatures up to 380° C and duration of pretreatment up to 4 h, although even up to 500° C leachability remained as high as 93 pct.

Table 5.—Aluminum leachability as function of pretreatment conditions

| Treatment duration and temp, °C	Leachability, pct	
	Confined gas under pressure	Flowing gas at ambient pressure
HELIUM ATMOSPHERE		
6 h:		
300	97.3	NAp
350	96.1	NAp
400	91.9	NAp
450	86.6	NAp
HYDROGEN		
6 h:		
160	96.7	NAp
180	96.9	NAp
200	96.8	NAp
220	97.1	NAp
240	96.8	NAp
260	96.9	NAp
280	96.6	NAp
300	94.4	NAp
320	89.1	NAp
340	85.0	NAp
360	80.0	NAp
380	70.2	NAp
4 h: 380	NAp	97.0
3 h: 500	NAp	93.0
2 h:		
380	NAp	97.0
400	NAp	95.0
1.9 h: 351	92.1	NAp
1.5 h: 450	NAp	93.0
1 h:		
300	NAp	97.0
380	NAp	97.0
0.9 h: 260	97.1	NAp
0.7 h: 339	97.5	NAp
0.6 h: 296	97.1	NAp
0.5 h: 380	NAp	97.0

NAp   Not applicable.
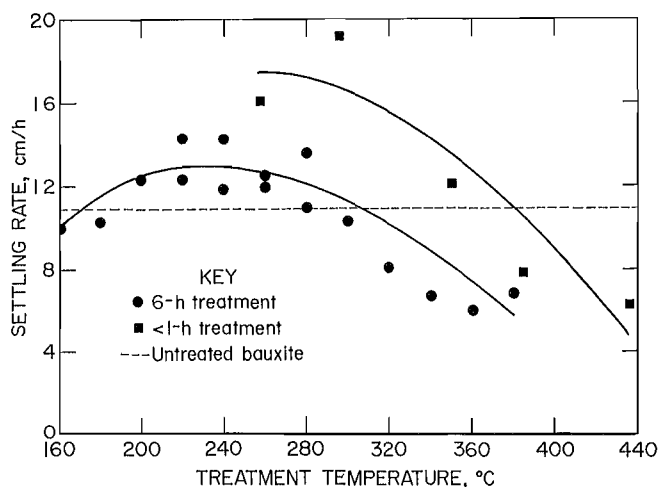
Figure 3.—Settling rate versus pretreatment temperature for leached residues from bauxite treated with hydrogen under pressure.
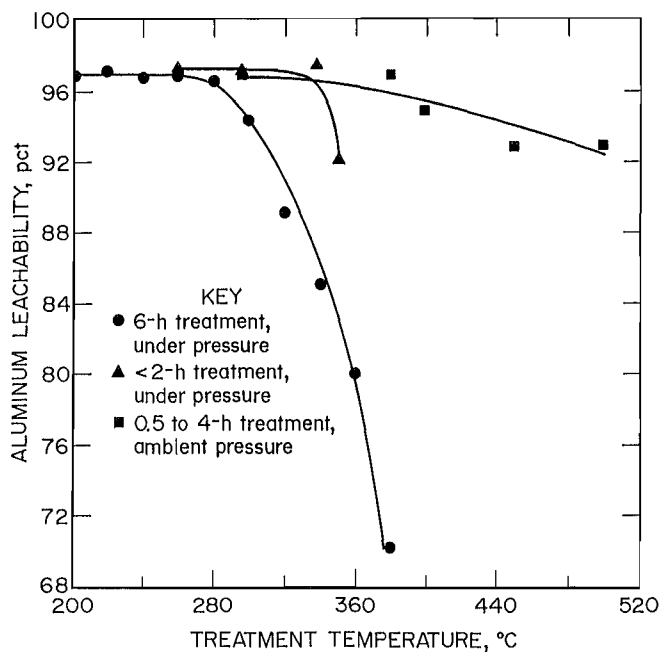

Figure 4.—Leachability of aluminum as function of hydrogen pretreatment temperature.

LEACHABILITY OF ORGANIC CARBON

The amount of organic carbon remaining in samples of residue after Bayer leaching was determined so that the amount of organic carbon carried into the leach liquor could be determined by difference. The objective was to seek conditions of pretreatment by which the amount of organic carbon imparted to leach liquor could be minimized, while not seriously impairing the leachability of aluminum. Figure 5 shows how the amount of organic carbon leached decreased relative to the amount of aluminum leached as the temperature of hydrogen pretreatment was increased. The amount of organic carbon leached from bauxite was decreased by pretreatment in hydrogen, and that benefit was obtained without significant sacrifice of aluminum leachability, provided the temperature of pretreatment was not excessive. For example, pretreatment in hydrogen under pressure for 6 h at 280° C decreased by more than 40 pct the amount of organic carbon leached, without loss of aluminum leachability.
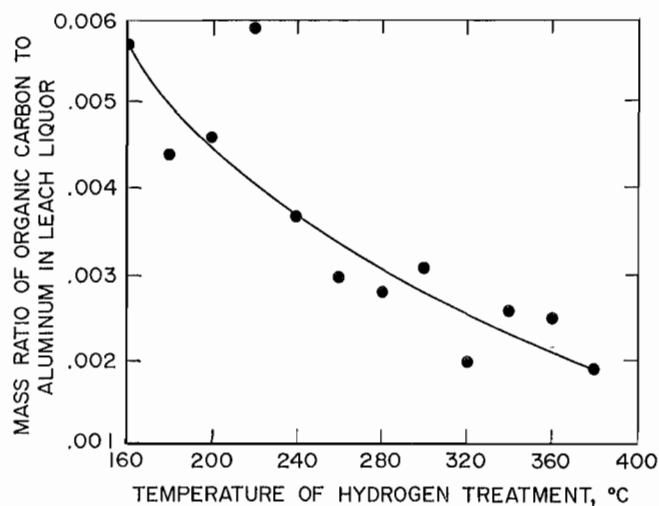

Figure 5.—Ratio of organic carbon leached to aluminum leached after pretreatment of bauxite in hydrogen under pressure.

MAGNETIC FILTRATION

Results of magnetic filtration applied to leached residues are tabulated in table 6.

Table 6.—Properties of solids fraction resulting from magnetic filtration

(Pretreatment in hydrogen under pressure for 6 h, except as noted)

Pretreatment temp, °C	Temp during magnetic filtration, °C	Solids fraction, pct			
		Slurry content		Retained[1]	
		Unwashed	Washed	Unwashed	Washed
Untreated	21	NA	14	NA	5
240[2]	21	NA	17	NA	47
240	21	NA	20	NA	10
260	21	48	29	9	6
280	21	39	30	24	9
300	21	48	22	67	34
320	21	42	25	87	82
340	21	46	30	100	100
360	21	58	32	100	100
380	21	48	34	100	100
380	90	48	34	100	100
380[3]	90	45	NA	100	NA
338[4]	90	34	NA	77	NA
338[2,4]	90	33	NA	75	NA

NA Not available.

[1]Solids retained in magnetic filtration apparatus, as a percentage of total solids introduced.

[2]Starch flocculant added before magnetic filtration.'

[3]>1-h duration of pretreatment.

[4]2-h duration of pretreatment.

Magnetic filtration of leached slurries from bauxite pretreated with hydrogen under pressure at temperatures from 340° to 380° C yielded a clear filtrate. Magnetic filtration of leached slurries derived from bauxite pretreated with hydrogen at temperatures lower than 340° C did not yield a clear filtrate.

Different degrees of dewatering of the magnetically filtered solids were obtained depending on whether the leached slurry was washed or not washed before being subjected to magnetic filtration. Magnetic filtration of leached slurries from bauxite pretreated with hydrogen at 340° to 380° C gave captured solids fractions with 30-pct solids content from washed slurry and with 50-pct solids content from unwashed slurry.

For pretreatment temperature of 380° C, even a brief duration at the elevated temperature produced a magnetic dewatering result as good as that achieved by 6-h duration. Effluent from magnetic filtration that appeared to be clear nevertheless did contain a small quantity of suspended solids, as demonstrated by careful filtration through a very retentive filter paper. Solids content of effluent obtained by magnetic filtration ranged from 1.5 to 1.9 mg/L.

MAGNETIC SEPARATION BY WET HIGH INTENSITY MAGNETIC SEPARATION

Results of WHIMS breakthrough tests on leached residues produced from bauxite which had been pretreated for 6 h in hydrogen under pressure are shown in table 7. From the experimental data appropriate values were determined for WHIMS operating conditions, i.e., specific flow rate and slurry loading, as functions of magnetic field strength and bauxite pretreatment temperature. The specific flow rate was found by dividing the flow rate through the magnetic cell by the cross-sectional area of the cell. This value was used to find the cross-sectional area of magnetic matrix required to clarify slurry introduced at a given flow rate. From these data, and the known 12.9-cm² cross-sectional area of a single magnetic matrix cell, it was possible to calculate the number of standard magnetic matrix cells required to handle a given flow rate of slurry. The specific effluent volume at breakthrough was found by noting the volume of leached bauxite residue that had passed through the magnetic matrix cell when the effluent quality reached approximately 10 mg/L solids and dividing by the cross-sectional area of the cell. These data were used to predict the volume of slurry that a standard matrix cell could receive before passing an excessive amount of solids. Predicted specific effluent volumes at breakthrough are shown in table 8.

Table 7.—WHIMS breakthrough results

Bauxite hydrogen pretreatment temp, °C	Field strength, G	Volume of slurry passed at breakthrough, mL	Suspended solids, mg/L
240	7,500	<10	>20
	10,000	<10	>20
	12,500	<10	>20
	20,000	<10	>20
300	5,000	200	10-15
	7,500	400	10-15
	2,500	460	10-15
	5,000	[1]700	7-10
	7,500	[1]700	3- 7

[1]Plugging of matrix occurred prior to breakthrough of solids.

Table 8.—Predicted WHIMS operating conditions[1]

Temperature at which bauxite was pretreated in hydrogen, °C	Field strength, G	Specific effluent volume at breakthrough, mL/cm²
240	20,000	([1])
300	5,000	15.5
	7,500	31.0
380	2,500	35.7
	5,000	54.3
	7,500	54.3

[1]Specific flow rate in all cases was 7.75 mL/min·cm².
[2]No significant retention owing to very low magnetic susceptibility at this pretreatment temperature.

To remove captured solids from the matrix, it was suggested by Eriez personnel that a WHIMS circuit with a matrix of grooved metal plates be used. Compressed air or steam could be used to blow the magnetic particles off the matrix. Bauxite pretreated with hydrogen at the near-optimal temperature of 380° C was used to produce leached residues for magnetic separation tests conducted at the Eriez laboratory. In their tests, compressed air was used to blow off the collected solids. Bauxite residue was sprayed onto the plates at field strengths up to 7,500 G. At 7,500 G, a maximum of approximately 45 pct of the solids was retained on the plates.

SETTLING RATES AND FILTRATION RATES OF LEACHED RESIDUES

Table 9 shows results of tests of the rate at which leached slurries settled, with and without flocculation. In every case, flocculation with starch was better than without, and when hydrogen pretreatment was used, higher pretreatment temperature gave a slower settling rate with

or without starch flocculation. When magnetic flocculation was used in addition to starch flocculation, settling rates of the residues from bauxite subjected to higher pretreatment temperature, i.e., the more magnetic residues, were enhanced by 20 to 30 pct over settling rates achieved by starch flocculation alone. Settling rate of a less magnetic residue was not enhanced by applying magnetic flocculation.

Filtration rates of leached slurries from bauxite pretreated in hydrogen under pressure at 380° C are shown in figure 6. Longer duration of hydrogen pretreatment gave the leached slurry a slower rate of filtration.

Table 9.—Settling rate of leached residues, measured at 90° C, centimeters per hour

Hydrogen pretreatment duration and temperature, °C	No flocculation	Starch flocculation	Starch and magnetic flocculation
None[1]	32	136	NA
0.7 h: 339	61	480	385
0.8 h: 381	26	393	466
6 h:			
240	98	325	NA
380	31	300	390

NA Not available.
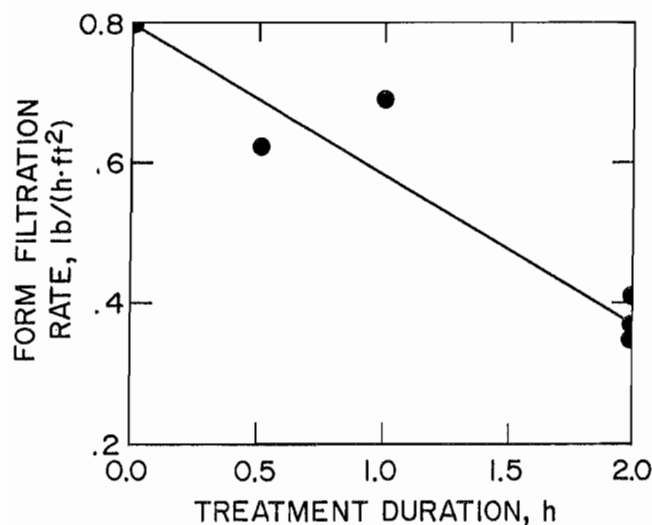[1]Residue from bauxite that was not pretreated.

Figure 6.—Effect of duration of hydrogen pretreatment on filtration rate of leached residue.

RESIDUES MADE MAGNETIC BY LEACHING WITH FeSO$_4$

A number of leaching and filtration tests were done in which addition of FeSO$_4$ during leaching was relied on to convert part of the bauxite's ferric iron to magnetite. The objective was to observe the effect of magnetite on the filterability of the leached residue. The effect of added FeSO$_4$ on the extent of leaching under standard conditions was also investigated. As shown by data in table 10, it proved to be very slight, except when an amount of FeSO$_4$ beyond the stoichiometric amount required for the reaction,

$$Fe_2O_3 + Fe^{2+} + H_2O \rightarrow Fe_3O_4 + 2H^+, \qquad (A)$$
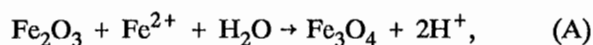
was used.

Residue from bauxite leached with added FeSO$_4$ filtered more rapidly than that from leaching without FeSO$_4$, as shown by filtration rate data in figure 7. The improved filtration rate held good over a four-fold range of initial slurry solids concentration.

Table 10.—Effect of ferrous sulfate addition on leachability of bauxite

Ferrous sulfate,[1] pct	Al extraction, pct	Ferrous sulfate,[1] pct	Al extraction, pct
0	96	40	99
	96	60	98
	97	80	95
	97	100	96
20	99	120	91

[1]Amount of FeSO$_4$ used relative to amount required to convert bauxite's ferric iron to magnetite.

PRETREATMENT IN HYDROGEN AT AMBIENT PRESSURE

Pretreatments of bauxite in flowing hydrogen at ambient pressure differed from those in static hydrogen under pressure, in that the flow of hydrogen carried away any moisture or other vapors evolved by bauxite when heated. It was thought that a loss of water vapor might diminish the bauxite's leachability or the filterability of its leached residue. As shown by data in table 11, the leachability was decreased only slightly, not as much as by 6-h pretreatment in hydrogen under pressure. However, as shown by data in table 12, in general, the rate of filtration of leached residue from bauxite pretreated in flowing hydrogen was inversely related to the duration of pretreatment, although aluminum leachability was not affected.
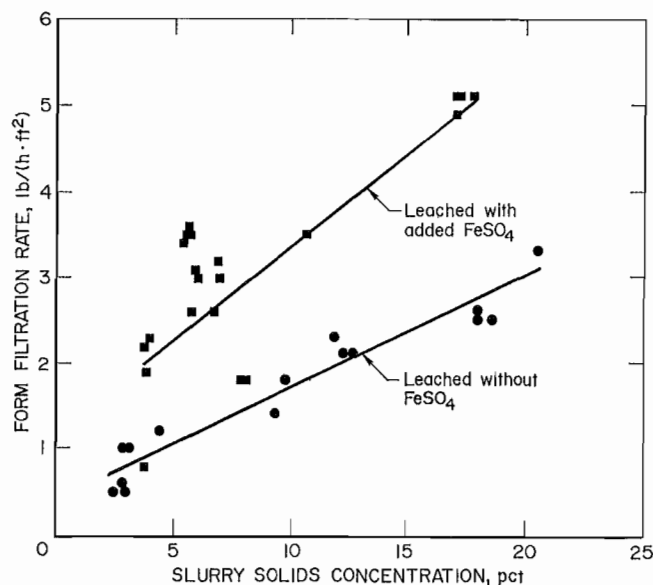
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Figure 7.—Effect of slurry solids concentration on filtration rate, for bauxite residues after leaching with and without added ferrous sulfate.

Table 11.—Effect of hydrogen pretreatment of bauxite at ambient pressure on leachability

Pretreatment duration, h	Hydrogen treatment temperature, °C	Al extraction, pct
1	300	97
2	400	95
1.5	450	93
3	500	93

Table 12.—Effect of duration of ambient-pressure hydrogen pretreatment on filtration rates of leached residue

Pretreatment duration,[1] h	Form filtration rate, lb/(h·ft^2)	Al extraction, pct
None	0.80	97.0
0.5	.63	97.0
1	.70	97.0
2	.35	97.0
2	.37	97.1
2	.41	97.0
4	.52	97.0

[1]380° C pretreatment temperature.

CONCLUSIONS

Pretreatment of a typical Jamaican bauxite with hydrogen at temperatures ranging from 160° to 500° C, with or without confinement under pressure, decreased its content of organic carbon and decreased the leachability of its organic carbon. Higher treatment temperature gave greater decrease of carbon content. Treatment at 320° C in hydrogen for 6 h decreased it by half. Only at pretreatment temperatures higher than 280° C was a decrease in aluminum leachability observed. Pretreatment of bauxite in hydrogen at temperatures higher than 160° C before leaching, preferably higher than 380° C, gave a decreased ratio of organic carbon to aluminum in the leach liquor. Pretreatment at 280° C decreased leachable organic carbon by more than 40 pct with no significant sacrifice of aluminum leachability. The decrease in leachability of organic carbon would allow a process using hydrogen-pretreated bauxite to be operated at a smaller recycle ratio, thereby consuming less energy per unit of alumina production, and would permit greater throughput for a plant of a given capacity.

Decarboxylation, i.e., decomposition of carboxylic acid functional groups, was responsible for a major part of the loss of organic carbon.

Pretreatment of bauxite with hydrogen at temperatures higher than 240° C made the bauxite and its leached residue partially magnetic, presumably by formation of magnetite, Fe_3O_4. A treatment temperature of 400° C produced the maximum level of magnetic susceptibility. Leaching untreated bauxite in the presence of added ferrous sulfate also produced a magnetic residue. Magnetic separation methods were shown to be effective in separating leached solids from leach liquor. Using magnetic separation would provide improved dewatering of leached residue, hence easier disposal of the dewatered residue; and would allow substitution of magnetic filtration for conventional filtration in the final polishing step, which would be conducive to higher purity in the alumina product.

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